Development of New C–N and C–P Bond Formations with Alkenes and Alkynes Based on Electrophilic Amination and Phosphination

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Abstract: Nitrogen and phosphorus are ubiquitously found in biologically active compounds, natural products, pharmaceutical agents, synthetic reagents, and even organic functional materials. The introduction of these heteroatoms into organic skeletons by the development of C–N and C–P bond forming reactions has been one of the long-standing research goals of synthetic chemistry. Both nitrogen and phosphorus have one lone pair, and synthetic chemists have therefore developed many nucleophilic amination and phosphination reactions. On the other hand, our research group has recently been focusing on the unique reactivity of hydroxylamines and hydroxylphosphines (tautomers of secondary phosphate oxides), and has developed otherwise challenging C–N and C–P bond–forming reactions with alkenes and alkynes based on electrophilic amination and phosphination using these reagents. In this account, we present an umpolung–enabled, copper–catalyzed, regio– and stereoselective aminoboration and hydroamination of alkenes, including unactivated terminal alkynes as well as electronically and sterically activated styrenes, strained alkenes, and vinyboranes/silanes. Additionally, a similar umpolung, electrophilic phosphophosphination of alkynes under Tf₂O–promoted, metal–free conditions is also described.

1. Introduction

Nitrogen (N)¹ and phosphorus (P)² are main group 15 elements that are ubiquitously found in natural products, biologically active compounds, and pharmaceutical agents. Additionally, they are frequently used in supporting ligands for transition metal catalysts, as well as being indispensable constituents of synthetic reagents in chemical synthesis. Moreover, many recently reported functional organic materials contain N and/or P as the key element. Hence, the development of C–N and C–P bond forming reactions that introduce amino and phosphino groups into organic skeletons has been one research area of long-standing interest to the synthetic community. Both N and P have one lone pair, and thus nucleophilic character. Therefore, synthetic chemists have developed numerous strategies using carbon electrophiles (organic halides, alkenes, and alkynes) and amine/phosphine nucleophiles (H(M)=N=NR, H(M)=PR₂), to achieve what are known as nucleophilic amination and phosphination of the type X=N=NR₁ (X = leaving group) can be a good alternative to the above nucleophilic amination. However, until 2010, the applicable carbon nucleophiles were mainly limited to highly reactive organometallic reagents such as organolithiums, –magnesiums, and –zincs.³ In this context, our research group has focused on the unique reactivity of chloroamines and hydroxylamine derivatives, and has recently developed the umpolung, electrophilic aminations of carbon nucleophiles of mild reactivity, including organoboranes, –silanes, ortho–alkynylphosphines/aminelines, and even aromatic C–H bonds (Scheme 1b).³ As part of our continuing interest in this chemistry, we next switched attention to the otherwise challenging C–N bond formation with alkynes based on electrophilic amination. In this account, we present a copper–catalyzed aminoboration of alkynes with diboron reagents and hydroxylamines: the boryl group and amino group are introduced as the boryl nucleophile and amino electrophile, respectively, and the corresponding β-borylalkylamines are formed in good yields with high regio– and stereoselectivity (Scheme 1c). The boryl nucleophile (diboron) can be replaced with a hydride nucleophile (hydroisilane), to achieve the net hydroamination of alkynes. Additionally, on the basis of a similar umpolung concept using hydroxylphosphines (tautomers of secondary phosphate oxide), a metal–free electrophilic phosphophosphination/cyclization of alkynes was developed, which is also described herein (Scheme 1d).


a) C–N and C–P bond formations with C electrophiles and N/P nucleophiles

b) our early examples of C–N bond formations with C nucleophiles and N electrophiles

(c) Cu–catalyzed aminoboration and hydroamination of alkynes with N electrophiles (this work 1)

d) metal–free phosphophosphination of alkynes with P electrophiles (this work 2)
2. Development of New C–N Bond Forming Reactions with Alkenes Based on Electrophilic Amination

2.1 Copper–Catalyzed Aminoboration of Alkenes

Organoboron compounds are an important class of compounds in modern organic synthesis because of their high utility for C–C and C–heteroatom bond formation, and they are used ubiquitously in the synthesis of complex natural products, biologically active compounds, and functional materials. Among the numerous approaches to organoboron compounds, transition–metal–catalyzed addition reactions of boron functionalities to C–C multiple bonds have recently received special attention. In particular, catalytic difunctionalization is strongly appealing because it enables the introduction of both boron and another functional group into organic molecules in one synthetic operation, and provides easy access to complex, densely functionalized organoboron compounds. However, until 2013 there was no report of successful simultaneous, densely functionalized organoboron compounds. Hence the development of a new catalytic system capable of aminoboration is highly desirable.

Meanwhile, in early studies on electrophilic amination we had found that some isolated organocopper complexes readily reacted with O-benzoylhydroxylamines to form C–N bonds even under mild conditions (Scheme 2). Based on this uniquely high reactivity of organocopper species towards hydroxylamine derivatives, we envisioned our blueprint for the catalytic aminoboration of alkenes through electrophilic amination (Scheme 3). Initial ligand exchange of a Cu(I) complex (Scheme 3) must occur with the organocopper intermediate (cis–1a) gave anti–3aa exclusively (Scheme 4a, left). Given the observed overall stereoselectivity of copper catalysis, the electrophilic amination (C to D in Scheme 3) must occur with retention of configuration. Particularly notable is the successful stereoinduction with an optically active (S,S)-Me–DuPhos ligand: the regio-, diastereo-, and enantioselective aminoboration of 1a with 2b was possible under CuCl(S,S)-Me–DuPhos catalysis, and 3ab was obtained in 83% yield with >99:1 syn:anti and 92.8 er (Scheme 4b).

Scheme 4. Copper–catalyzed aminoboration of styrenes.

The copper–catalyzed aminoboration reaction was applicable to several strained alkenes (Scheme 5). In the case of methyleneacyclopropanes 4, the amino group and boryl group were guided to the internal position and terminal position, respectively, and the corresponding borylmethyl–substituted cyclopropylamines 5 were obtained in good yields with high trans diastereoselectivity (Scheme 5a). The product obtained, for example 5aa, can undergo further transformations based on the rich chemistry of Bpin: one–carbon homologation followed by oxygenation, amination, and Suzuki–Miyaura cross-coupling afforded the functionalized cyclopropylamines 6–8 in acceptable yields. The parent structure of 6–8, namely, trans–2–phenylcyclopropylamine, is also known as Tranelyproline and has unique biological activity. Thus aminoboration

generates borylcopper species B. Subsequent insertion of the alkene into the Cu–B bond of B furnishes a borylated alkylcopper intermediate C. The umpolung electrophilic amination with the O–benzoylhydroxylamine then occurs, forming the desired aminoborated product and L,CuOBz complex D. Final salt metathesis with MO–t–Bu regenerates A to complete the catalytic cycle. Providing the reaction of B with the alkene proceeds preferably even in the presence of the O–benzoylhydroxylamine, chemoselective aminoboration can be realized.
catalysis can provide a useful building block for the synthesis of a variety of Tranylcypromine derivatives. The oxygen–nitrogen– and simple methylene–bridged bicyclic alkenes were also viable substrates (Scheme 5b). With the chiral CuCl/(R,R)-Ph-BPE catalyst, the exo- and enantioselective aminoboration reaction proceeded to furnish the chiral aminoborated products in good yields with 89:11–96:4 er.

Scheme 5. Copper–catalyzed aminoboration of strained alkenes. Conditions: a) NaBO2·H2O, THF/H2O, rt. b) BuLi/MeONH2, THF, 60 °C, then Boc2O, rt. c) Pd(OAc)2/RuPhos (10 mol%), CsOH·H2O, PhBr, 1,4-dioxane/H2O, 100 °C.

Unactivated terminal olefins are simple and abundant bulk commodities, and at present more than 1,600 such compounds are commercially available from various suppliers. The derivatization of these feedstock materials is thus of great importance in organic synthesis. The aforementioned aminoboration copper catalysis can also be applied to an unactivated terminal alkene 11 (Scheme 6a). Additionally, a unique, ligand–controlled regioselective aminoboration with pinB–Bpin proceeded to furnish the chiral aminoborated products in good yields with 89:11–96:4 er.

Scheme 6. Copper–catalyzed aminoboration of unactivated terminal alkenes. The ratio is that of the regioisomers.

2.2 Copper–Catalyzed Hydroamination of Alkenes

Following the above success of the aminoboration reaction, we next designed a net hydroamination reaction of
alkenes by using a hydrosilane instead of the diboron reagent (Scheme 7): if the hydrosilane works as an efficient hydride source for the copper salt (A’ to B’), and alkene insertion into the Cu–H bond occurs preferably over the reaction of the latter with the hydroxylamine (B’ to C’),21 the familiar electrophilic amination of the alkylcopper intermediate (C’ to D’) would deliver the hydroaminated product.


In fact the regio- and enantioselective hydroamination of styrenes 1 proceeded in the presence of a CuCl(S,S)-Me-DuPhos catalyst to deliver the optically active benzylicamines 14 in good yields with high enantioselectivity (Scheme 8).24 The less expensive and readily available polymethylhydrosiloxane (PMHS) operated effectively as the hydrosilane. In some cases, the (R,R)-Ph-BPE ligand gave better enantioselectivity, although the exact reason for this is not clear. Particularly notable is the successful enantioselective hydroamination of β-substituted styrenes: these substrates are inaccessible using the conventional enantioselective, nucleophilic hydroamination catalysts.25

Scheme 8. Copper-catalyzed hydroamination of styrenes. The ligand used is in parentheses.

The reaction mechanism of hydroamination with hydrosilane and hydroxylamine is completely different from that of the conventional hydroamination catalysts, and thus otherwise challenging substrates can also be accommodated. The bicyclic alkene 9 is such a case, and enantioselective hydroamination effectively occurred under CuCl/(R,R)-Ph-BPE asymmetric catalysis (Scheme 9).26 Similarly to the examples shown in Scheme 5b, the oxygen- and nitrogen-bridged bicyclic alkenes 9 took part in the reaction to afford the optically active amines 15. While somewhat dependent on the solvent, good to high enantioselectivity was observed. In addition, no byproducts associated with a ring-opening side reaction were detected at all.27

Scheme 9. Copper-catalyzed hydroamination of bicyclic alkenes. The solvent used is in parentheses.

We note that the research group of Buchwald independently developed a similar copper-catalyzed hydroamination and successfully extended the scope to even more challenging unactivated internal alkenes.28 One example is illustrated in Scheme 10.

Scheme 10. Copper-catalyzed enantioselective hydroamination of unactivated internal alkenes developed by Buchwald.

2.3 Application to Synthesis of α-Aminoboronic Acids and α-Aminosilanes

α-Aminoboronic acids and α-aminosilanes are boron and silicon analogues of α-amino acids and thus frequently found in bioactive molecules. Some well known examples include Bortezomib, Ixazomib, angiotensin-converting enzyme (ACE) inhibitor, and serine protease neutrophil elastase (HNE) inhibitor (Figure 1).29 The greatest synthetic challenge with these molecules is the control of point chirality at the carbon between B (Si) and N, and in this context catalytic stereindention still remains underdeveloped. We hypothesized that if the catalytic hydroamination mentioned above was applicable to a boron-substituted alkene with the desired control of enantioselectivity as well as selectivity, the corresponding optically active α-aminoboronic acid derivative could be formed catalytically. On the basis of this assumption, we developed the regio- and enantioselective hydroamination of BdAn-substituted alkenes 16 in the presence of a Cu(OAc)2/(R)-DTBM-SEGPHOS catalyst (Scheme 11a).30 The asymmetric copper catalysis accommodated both alkyl- and aryl-substituted alkenes, and the corresponding α-aminoboronic acids 17 were
obtained in good yields with high enantioselectivity. Additionally, the absolute configuration of the thienopiperidinyl derivative prepared was successfully assigned to be R by a single crystallographic X-ray analysis. In most cases the regioselectivity was also perfectly controlled: this is determined in the insertion step of 16 into the Cu–H species (Scheme 7) with the assistance of hyperconjugation between the Cu–C σ bond and the empty p orbital on boron. Moreover, the related aminoboration of 16 was also possible, although the enantioselectivity still remained to be improved (Scheme 11b).

Figure 1. α-Aminoboronic acids and α-aminosilanes in bioactive molecules.

Scheme 11. Copper–catalyzed enantioselective hydroamination and aminoboration of boryl–substituted alkenes for the synthesis of chiral α-aminoboronic acid derivatives.

The vinylsilane 19a also underwent regio- and enantioselective aminoboration in the presence of CuO(OTf)·2H2O and (R,R)-Ph–BPE (Scheme 12). After treatment with H2O2 aq., the corresponding β-hydroxy-α-aminosilane 20aa-O, a kind of serine mimic, was formed in 70% yield with 96:4 er. Again, hyperconjugation, was the Cu–C σ orbital and proximal Si–C σ* orbital might effectively influence the insertion step (Scheme 7) to deliver the single regioisomer observed. We also note that Buchwald developed an enantioselective hydroamination of vinylsilanes, leading to a diverse set of optically active α-aminosilanes with high enantioselectivity.

3. Development of New C–P Bond Formations with Alkynes Based on Electrophilic Phosphination

3.1 Tf2O–Promoted Phosphinative Cyclization of Alkynes

“What are the most commonly used electrophilic phosphination reagents?” Maybe, many synthetic chemists would answer “chlorophosphines”. Indeed, they readily react with organometallic reagents such as organolithiums and organomagnesiums even in the absence of any catalysts to furnish the corresponding tert-phosphines (Scheme 13a). On the other hand, their electrophilicity toward simple aromatic hydrocarbons (e.g., benzene) is insufficient: the reaction of trichlorophosphate with a solvent amount of benzene occurs only under harsh conditions (600 °C), and the product selectivity is not very high (Scheme 13b). However, how are we to prepare more reactive and more electrophilic phosphination reagents? We envisioned that a phosphorus analogue of the O-acylated hydroxylamine mentioned in Section 2 might show remarkably high electrophilicity under suitable conditions (Scheme 14a). Our reaction design is shown in Scheme 14b. The hydroxylphosphine, a tautomer of readily prepared and stable secondary phosphine oxide 21, is activated with a suitable acylation reagent to form the O-acylated hydroxylphosphine in situ. If this species is sufficiently electrophilic to serve as a phosphonium cation equivalent, a [2+1] cycloaddition with alkyne 22 could occur to generate a three–membered phosphirenium cation intermediate. This process can be regarded as a cyclopropanation because the phosphonium cation is isoelectronic to a carbene. A final ring-opening with the pendant nucleo-

Scheme 12. Copper–catalyzed regio- and enantioselective aminoboration of vinylsilane for the synthesis of a chiral α-aminosilane.

Scheme 13. Traditional electrophilic phosphination reactions with chlorophosphines.

Scheme 14. Our working hypothesis and reaction design.
phile of the alkyne then affords the phosphinative cyclization product 23.

With the above working hypothesis in mind, we started optimization studies with the NTs–tethered alkyne 22a (phenyl ring as the pendant nucleophile) and diphenylphosphine oxide (21a). While mild acylating reagents such as Ac₂O, Ts₂O, and (CF₃CO)₂O failed to promote the reaction, a combination of sulfonation reagent Tf₂O and 2,6-lutidine was found to form the desired 23aa successfully with no requirement for additional catalyst (Scheme 15). We confirmed the initial formation of P (III) product by ³¹P{¹H} NMR, but for ease of handling, the corresponding air–stable phosphine oxide 23aa–O and sulfide 23aa–S were isolated after treatment with H₂O₂, aq and S₈, respectively. The conditions established were effective for the reaction of various alkynes 22 and secondary phosphine oxides 21. Representative products are illustrated in Figure 2. In addition to the NTs–linked 22a, the oxygen, sulfur, ester, methylene, and phenylene tethers worked well, and the corresponding phosphinative cyclization products were formed in good to high yields (23ab–O, 23af–O). A DTBM–type phosphine oxide and cyclic phosphinate ester were also viable phosphate donors (23bg–O and 23cg–O). Nitrogen and oxygen heteroatoms could also be employed as the pendant nucleophile to deliver the corresponding β-phosphinylheterocycles 23ah–O, 23aj–O in acceptable yields. Moreover, even a simple alkene successfully participated in the reaction to produce the tricyclic system 23ak–O in good yield.

Scheme 15. Optimal conditions for phosphinative cyclization of alkynes with secondary phosphate oxides via electrophilic phosphination. The bonds formed are indicated with bold lines.

On the basis of the above findings, we propose the following mechanism for the reaction of 21a with 22a (Scheme 17). The electrophilic phosphorus species E generated from the tautomer of 21a and Tf₂O undergoes [2+1] cycloaddition with alkyne 22a to form the phosphinonium cation F. The alkyne 22a has a pendant nucleophilic aryl moiety at the appropriate position, and arylation–opening of the phosphinonium cation thus occurs to furnish the phosphinative cyclization product 23aa. We could not directly observe the phosphinonium cation corresponding to E, but such a species is believed to be involved as the key intermediate in the present reaction.

Scheme 17. Plausible mechanism for reaction of 21a with 22a.

3.2 Phosphonium Cation Mediated Cycloaddition Approach to Benzophospholes

Benzophosphole derivatives have received significant attention in the field of material chemistry research because of their unique optical, electronic, and physical properties, as exemplified by impressive applications in organic light–emitting diodes, photovoltaics, and cell imaging dyes. Thus, while protocols for their synthesis have been studied, there still remains a strong demand for more concise and rapid preparations of these compounds, since most reported procedures suffer from tedious multistep sequences, toxic and unstable substrates/ reagents, and poor functional group compatibility. In 2013, our group and Duan independently reported a silver– or manganese–promoted oxidative formal [3+2] cycloaddition approach to benzophospholes from secondary phosphate oxides and internal alkynes (Scheme 18a). The reaction can construct the benzophosphole skeleton readily from two simple, stable organic components. However, the intermediacy of a radical causes nonselective rearrangement to form a nearly 1:1 regioisomixture of usual and rearranged products when any substituted arylphosphine oxides, even para–substituted ones,
are employed. This issue of regioselectivity hampers wide application of this strategy to the synthesis of benzophospholes.

Scheme 18. Formal [3+2] cycloaddition approach to benzophospholes from secondary phosphine oxides and internal alkynes.

During the mechanistic study shown in Scheme 16, we serendipitously discovered a unique behavior of phosphirenium cation 25: the corresponding benzophosphole oxide 27aa was formed when the reaction mixture was simply heated to 100 °C (Scheme 18b). This phenomenon prompted us to optimize the conditions for synthesis of the benzophosphole. We were pleased to find that Tf₂O/DMAP effectively promoted formal [3+2] cycloaddition of diphenylphosphine oxide (21a) and diphenylacetylene (24a) in heated DCE to produce 27aa in 87% yield (Scheme 19).² The initially formed P(III) benzophosphole was spontaneously partially oxidized to the corresponding oxide 27aa with residual Tf₂O (vide infra), but upon workup we added H₂O₂ aq. to complete the oxidation. The salient feature of this process is regioselectivity in the reaction of para- or meta-substituted phosphine oxide 21; for example, the para-tert-butyl-substituted arylphosphine oxide 21d was selectively converted to the rearranged benzophosphole 27da as the single regiosomer shown. The same unique regioselectivity was observed when using ortho-methoxy- and bromo-substituted phosphine oxides (27ca and 27fa). The structure of 27fa was unambiguously confirmed by X-ray analysis.

Scheme 19. Phosphenium cation-mediated formal [3+2] cycloaddition approach to benzophospholes from secondary phosphine oxides and internal alkynes.

Useful mechanistic insight into the C–P rearrangement process was obtained from ³¹P{¹H} NMR studies with dimethylphosphine oxide (21h), in which all the possible reactive ortho sites are blocked by methyl substituents (Scheme 20). The corresponding phosphirenium cation 28 (δ = -126.8 ppm) was immediately observed at 60 °C, but the C–P rearranged vinylphosphine oxide 29 (δ = -126.8 ppm, JPH = 499 Hz) was finally isolated after an additional 12 h at 120 °C. This finding suggests that apparently the aryl group transfer from phosphorus to vinylic carbon in the phosphirenium cation occurs prior to formation of the benzophosphole skeleton.

Scheme 20. ³¹P{¹H} NMR studies with dimethylphosphine oxide (21h).

On the basis of the above outcomes, we are tempted to propose that the mechanism of reaction of 21a with 24a is as follows (Scheme 21). As illustrated in Scheme 17, the highly electrophilic phosphonium cation E is initially formed via the tautomerization of 21a. Subsequent [2+1] cycloaddition with 24a (E to 25) is followed by phenyl group migration from phosphorus to vinylic carbon to generate a vinylphosphonium cation G. An intramolecular phospha–Friedel–Crafts reaction then occurs to construct the benzophosphole framework. Thus, even the para- and ortho-substituted arylphosphine oxides (27da–27ga in Scheme 19) can be converted to the C–P rearranged single isomers. The initially formed P(III) benzophosphole is readily oxidized with residual Tf₂O to form the observed benzophosphole oxide 27aa.⁴³

Scheme 21. Plausible mechanism for reaction of 21a with 24a.

4. Conclusion

We have focused on the unique reactivity of hydroxylamines and hydroxyphosphines (tautomers of secondary phosphine oxides) and utilized them in the development of several new C–N and C–P bond forming reactions of alkenes and alkynes based on electrophilic amination and phosphination. The hydroxylamine works as an N electrophile under suitable Cu catalysis and enables otherwise challenging catalytic amination and hydroamination of various alkenes. Additionally, applications to asymmetric catalysis, as well as synthesis of B and Si analogues of α-aminoacids can be achieved. In the electrophilic phosphination, Tf₂O uniquely allows the hydroxylphosphine to serve as a highly reactive P
electrophile (a phosphonium cation equivalent), and phosphoni-
native cyclization of alkynes containing pendant nucleophiles proceeds even under metal–free conditions. The TfO–promoted protocol is also applicable to the regioselective synthesis of benzophospholes from readily accessible and simple start-
substrates. The key to these successes is the realization of umpolung, electrophilic amination and phosphinization strategies.

Further applications of related electrophilic amination/phosphinization methodologies in chemical synthesis and the development of conceptually new umpolung chemistry are currently underway and will be reported in due course.

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We confirmed the rapid conversion of independently prepared P(III) benzophosphine to benzophosphine oxide in the presence of Ti(O.)